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Revision of Emission Factors for Petroleum Refining

Radian Corp, Austin, Tex

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REVISION OF EMISSION FACTORS FOR PETROLEUM REFINING

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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16. ABSTRACT

The refinery air pollutant emission factors presently contained in Section 9.1 of AP-42, A Compilation of Air Pollutant Emission Factors are primarily based on the results of the Los Angeles Joint Project conducted from 1955 to 1958. Since that time there have been many process and equipment developments in the petroleum refining industry. There have also been several individual and control agency emission testing programs for refinery emission sources. This report presents the results of an in-depth study to revise and update the emission factors and process descriptions presented in AP-42 for the petroleum refining industry. The revisions were to be made only using available information. A testing strategy was also developed for testing refinery emission sources where further source testing is warranted.

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1.0 SUMMARY

The program conducted by Radian in support of EPA's Office of Air Quality Planning and Standards is summarized here in Section 1. Radian provided assistance to the EPA in the following two task areas:

1) Process descriptions and emission factors presented in the petroleum refinery section of EPA document AP-42 were reviewed and expanded.

2) A testing strategy for refinery emission sources with inadequate emission factors was developed.

1.1 Process Description Review of AP-42

- The general descriptions of petroleum refining objectives and the major processes used to achieve these objectives were expanded.

- Detailed process descriptions were prepared for fourteen major refinery emission sources. These descriptions were accompanied by a discussion of emission characteristics and applicable emission control technology.

1.2 Emission Factor Review of AP-42

- Corrections, adjustments, and additions were made to a major portion of the non-fugitive emission factors.

- Fugitive emission factors were assembled into a separate table. The fugitive emission factor table lists emission factors for controlled sources as well as emission factors for uncontrolled sources.

- Where available, fugitive emission factors are reported in more than one set of units to add to their utility.

- Where recent information indicated emission factors were outdated, the emission factor accuracy ratings were lowered appropriately. Where before all factors were rated A, most are now rated B and C. Fugitive emission factors were given a general rating of D.

1.3 Test Plan Development

- It was recommended that four refinery emission sources be given high priority for emission testing programs: fugitive, storage, blowdown, and vacuum distillation column condensers. A significant improvement can be gained in the emission factor accuracy for fugitive, blowdown, and vacuum distillation column condenser sources. Less improvement can be gained for storage emission factors, but the magnitude of storage emissions makes this improvement significant also.

- Three refinery emission sources were given an intermediate priority status: loading operations, internal combustion engines, and fluid coking units. Emission factors for loading operations are good, but the large volume of loading losses makes their inaccuracies significant. Internal combustion engine factors are of less importance because internal combustion engines are being phased out of use in the refining industry. Fluid coking emissions are small nationally, (≈16% of the coking capacity) but will become more important if the use of the process increases.

- Five emission sources were given low priority status for testing programs because of their low potential for significant accuracy improvements: boilers, heaters, fluid catalytic crackers, moving bed catalytic crackers, and sulfur recovery plants. Boilers and heaters have excellent emission factors. Although emission factors are not as good for fluid catalytic crackers, moving bed catalytic crackers, and sulfur recovery plants, these factors are not easily improved because their inaccuracies are attributed to variations in undefined process parameters.

- The estimated cost for sampling point source emissions is $100,000 per source category. A fugitive emission source testing program is estimated to cost a total of $1,400,000. It has also been estimated that tankage emission sources might be tested for $750,000. It should be noted

that a broad study to characterize fugitive emissions from petroleum refineries is currently underway. The study is being conducted by Radian Corporation for the Industrial Environmental Research Laboratory of EPA, and includes the testing of emissions from eleven categories of fugitive emission sources in sixteen refineries.

2.0 INTRODUCTION

Between 1955 and 1958 a task force consisting of petroleum companies and air control agencies conducted the Los Angeles Joint Project to determine the air emissions from petroleum refining operations. The refinery air emission factors presently contained in Section 9.1 of AP-42, A Compilation of Air Pollutant Emission Factors are based largely on this study. However, there have been many technological improvements since 1958, and there have been many individual efforts to obtain emission source testing data for the various processes and equipment in refineries. Therefore, the objectives of this study were 1) to revise the emission factors and process descriptions presented in AP-42 for refinery operations using available information, and 2) to develop a comprehensive testing strategy for emission sources where further source testing is warranted.

The process descriptions were written to give a clear understanding of overall refining activities with emphasis placed on significant emission sources. The emission factors were updated where possible. The revised factors reflect improved technology and recent source testing data.

Having achieved an overview of the available source testing data, a comprehensive testing strategy was developed for sources where further testing is needed. The strategy development included an analysis of difficulty in testing, relative emission contribution, available data, and accuracy of the present factor.

3.0 REVISION OF AP-42; SECTION 9.1, PETROLEUM REFINERIES

The major objective of this program was the development of improved emission factors and process descriptions for the petroleum refining industry. These improved factors and descriptions comprise the revisions to the petroleum refining section of EPA Document AP-42, Compilation of Air Pollutant Emission Factors. Section 3.1 discusses the data gathering operations conducted by Radian for this program. Section 3.2 discusses the development of improved process descriptions and Section 3.3 presents the methodologies used by Radian to update the refinery emission factors. And Section 3.4 reviews the testing information transmitted to Radian from the EPA. The revised Section 9.1 of AP-42 on refinery emission sources is presented in Appendix A.

3.1 Data Gathering Operations

To update the emission factors and process descriptions for petroleum refineries contained in AP-42, it was necessary to obtain all available information pertaining to petroleum refining processes and emissions. Because this project concerns both the processing and environmental aspects of refining, information covering a broad range of topics was gathered. Topical areas included general refinery technology information, specific process data, and emission control technologies. Sources of information were government agency reports, federal and state publications and support documents, technical papers, journals, industry news releases, process design data, previous and current Radian studies, and contacts with government and industrial personnel associated with petroleum refining and its emissions.

Information was gathered from the literature by using computer assisted information services. The literature search involved preliminary machine searches to several on-line abstracting services, including Petroleum/Energy Business News Index, Chemical Abstracts, NTIS/Governmental Reports Announcements, and Engineering Index. Chemical Abstracts and Engineering Index provided the most useful information. Therefore, searches were made of these two data bases using the broad terms "Petroleum Refining", "Petroleum Products", "Refinery Emissions", "Refinery Effluents", and "Refinery Wastes". Both data bases were subsequently searched for the various refinery processes. All searches were completed for the time period of 1972 to the present. Previous studies conducted by Radian Corporation had extensively covered all data generated prior to 1972 on the subject of refinery processes and emissions. This data was available to the project through the Radian library. Printouts of titles obtained from Chemical Abstracts and abstracts obtained from Engineering Index were scanned, and the pertinent articles and/or abstracts were acquired.

Personnel in both industry and government were contacted in an effort to obtain the latest information regarding refinery processes, emission studies, and control technologies. Table 3.1-1 lists the contacts made by Radian and reviews the content of the discussions. As the table shows, very few refinery emission studies have been made recently. There are several parallel studies currently underway or recently completed. These studies include investigations of emissions from offshore platforms, tankers, tankage, and marketing. However, no appreciable refinery emission source testing data is available at this time. Chuck Masser of EPA has furnished source testing data for process heaters and boilers. PES had some refinery source testing data that could not be released to us in time for use in this study due to regulations concerning the confidentiality of the data.

TABLE 3.1-1. INDUSTRY CONTACTS

Name and Affiliation	Address and Phone	Subjects, Comments
KVB		
Steve Cherry	17332 Irving Tustin, Calif. 92680 (714) 832-9020	1) No refinery emission data available other than what EPA had already transmitted to Radian Corporation.
EPA - National Emissions Inventory		
Charles C. Masser	EPA, OAQPS, MDAD, AMTB, SAS Room 526, Mutual Bldg. MD-14 Research Triangle Park, North Carolina 27711	1) Supplied emissions data for process heaters and boilers. 2) Supplied NEDS inventories.
EPA - Division of Stationary Source Enforcement		
Jim Casey	Washington, D.C. (202) 755-7927	1) Confidential refinery source test results which can't be released within the time limits of our study. Some question also existed on usefulness of the data.
Pacific Environmental Services		
Artie Stein	1930 14th St. Santa Monica, Calif. 90404 (213) 393-9449	1) Have done no testing of refinery emission sources. 2) Have received some industry source test results from industry as a result of their National Survey of Refineries study; but are confidential.

(Continued)

TABLE 3.1-1. INDUSTRY CONTACTS (Continued)

Name and Affiliation	Address and Phone	Subjects, Comments
EPA - Chemical and Petroleum Branch Kent Hustvedt	Research Triangle Park, Durham, N.C. 27711 (919) 541-5371	1) No new refinery emissions data available to his knowledge.
API - Division of Environmental Affairs Edward Crockett	1801 K St. N.W. Washington, D.C. (202) 457-7084	1) They have canvassed all members about available test data this year. No appreciable refinery emissions data was turned up.
Western Oil and Gas Association Bob Harrison	Los Angeles, Calif. (212) 486-7538	1) WOGA is not conducting any studies on refinery emissions sources. 2) WOGA is presently studying emissions from tanker operations, floating roof tanks, and cone roof tanks.
EPA - Chemical and Petroleum Branch Dick Burr	Research Triangle Park, Durham, N.C. 27711 (919) 541-5371	1) No new emissions data.
Union Oil Edward Bloom Dick Salsbury	Los Angeles, Calif. (213) 486-7538	1) WOGA has plans to conduct refinery tests. 2) No current emissions data.

(Continued)

TABLE 3.1-1. INDUSTRY CONTACTS (Continued)

Name and Affiliation	Address and Phone	Subjects, Comments
ARCO - Production Engineering Department John Hundley, Jr.	Bakersfield, Calif. (305) 831-1600	1) ARCO has not conducted any refinery emission tests. 2) ARCO has data on emissions from production equipment.
California Air Resources Board Jim Leach	Sacremento, Calif. (916) 322-2745	1) No recent refinery emission studies. Earlier data by KVB already transmitted to Radian.
Santa Barbara County Health Department John Laird	Santa Barbara, Calif. (805) 967-2311	1) No refinery emission studies. 2) Test data on emissions from offshore platforms.
ARCO Harvey Grimes	Harvey, Illinois (312) 333-3000	1) No refinery emission studies. 2) Marketing loss studies only.

3.2 Development of Improved Process Descriptions

The process descriptions were written with two main objectives. The first objective was to present a clear picture of overall refining activities. The second was to emphasize those refining processes which are the major sources of air emissions. To accomplish these objectives it was necessary to describe the processes in sufficient detail to clearly define the process flows, major equipment items, and emission sources. The descriptions included updated process information. It was further necessary, because of space limitations, for the process descriptions to be concise.

The description of the petroleum refining industry was organized in the following manner:

1) statement of the refinery's overall objective,

2) definition and description of five general process categories, and

3) definition and description of specific processes that are significant air pollutant contributors.

The overall refinery description discusses products, feedstocks, and objectives, and presents the diagram of an example refinery flow scheme.

The individual refinery processes are categorized as separation processes, conversion processes, treating processes, product handling, and auxiliary facilities. The descriptions of these five categories of processes discuss the products, feedstocks, and objectives of the processes within the category.

Detailed descriptions are presented for the specific refinery processes that are significant air pollutant contributors. These descriptions include products, feedstocks, processing objectives, process flows, emission sources, and applicable control technology.

Refining processes that are significant sources of air pollutants are emphasized. The description of these processes are more detailed than the descriptions presently contained in AP-42. The expansion of the process descriptions should enable a clearer understanding of the process and its emission sources. Objectives, feedstocks and products are discussed. A process flow scheme is presented to allow a clear understanding of the process. Operating conditions (*e.g.*, high temperature and pressure) and equipment (*e.g.*, process heaters and catalyst regenerators) important to considerations of air pollutant sources are emphasized. Finally, the types of air pollutants, emission sources, and applicable control technology are discussed.

The sources of information for these descriptions are recent texts, journals, periodicals, and Radian reports. In general, specific process descriptions were based on the most widely used process. Where two or more processes are in wide use either two separate descriptions are included, or a generalized description encompassing both processes is included. Although refining processes are complex and unique to the specific refinery needs, the generalized process descriptions do allow an understanding of the process flows and the basic processing equipment involved.

3.3 Emission Factor Review and Update

As part of the revision of EPA Document AP-42, Radian reviewed and updated the emission factors presented in AP-42 for refinery emission sources. Generally, this review and update was based on information collected by Radian from an extensive literature search and through contacts with the petroleum industry and air control agencies. In this section the revisions made by Radian to the refinery emission factors and the basis for the revisions are presented. Information gathering methods were discussed in Section 3.1. The revised refinery section of AP-42 is presented in Appendix A. Table 3.3-1 summarizes which emission factors were changed, and for what reasons. Section 3.4 reviews the testing information transmitted to Radian from the EPA.

3.3.1 Boiler and Heater Emission Factors

Changes were made to both the carbon monoxide emission factors and the hydrocarbon emission factors currently reported in AP-42 for refinery boilers and heaters. The Los Angeles Joint Project, upon which the existing refinery boiler and heater emission factors were based, found the carbon monoxide emission rates to be negligible (AT-040). However, later studies conducted by EPA and Southwest Research Institute identified the level of carbon monoxide from industrial boilers to be 210 lbs/1000 bbl oil burned or 17 lbs/10^6 ft^3 gas burned (EN-071 Section 1.3 and 1.4). Since refinery heaters operate under similar conditions to refinery boilers, Radian assumed the carbon monoxide rate for the two to be similar. The refinery boiler and heater carbon monoxide emission rates were changed from negligible to the above values.

TABLE 3.3-1. SUMMARY OF EMISSION FACTOR REVISIONS

Emission Source	Pollutant	Original Value	Revised Value	Reason and Source of Change
Boilers & Heaters	CO	Negligible	210 lbs/1000 bbl	Studies by EPA & SwRI (EN-071 Sec. 1.3 & 1.4)
	HC	140 lbs/1000 bbl 0.03 lbs/1000 ft^3	42 lbs/1000 bbl 0.003 lbs/1000 ft^3	
Cat. Cracker w/CO boiler	HC	220 lbs/1000 bbl	Negligible	Based on a review of incinerator impact on these pollutants.
	Aldehyde	71 lbs/1000 bbl	Negligible	
Fluid Coker Uncontrolled	CO	Negligible	Not available	These pollutants were not investigated in the sources quoted.
	HC	Negligible	Not available	
	NO_x	Negligible	Not available	
	Aldehydes	Negligible	Not available	
	Ammonia	Negligible	Not available	
Fluid Cokers w/CO boilers	NO_x	Negligible	Not available	These pollutants were not investigated in the sources.
Reciprocating Compressor Engines	CO	Negligible	0.43 lbs/1000 ft^3	Later studies by SwRI developed these revised emission factors (EN-071 Sec. 3.3) based on extensive testing.
	HC	1.2 lb/1000 ft^3	1.4 lbs/1000 ft^3	
	NO_x	0.9 lb/1000 ft^3	3.4 lbs/1000 ft^3	
Gas Turbine Compressor Engines	SO_x	None	2s lbs/1000 ft^3	These factors did not previously appear in this table. Based on SwRI studies (EN-071 Sec. 3.3)
	CO	None	0.12 lbs/1000 ft^3	
	HC	None	0.02 lbs/1000 ft^3	
	NO_x	None	0.3 lbs/1000 ft^3	
Blowdown System uncontrolled	HC	300 lbs/1000 bbl	580 lbs/1000 bbl	Lockheed Study including more extensive testing (KL-081)

(Continued)

TABLE 3.3-1. SUMMARY OF EMISSION FACTOR REVISIONS (Continued)

Emission Source	Pollutant	Original Value	Revised Value	Reason and Source of Change
Blowdown system controlled w/flare	SO_x	None	26.9 lb/1000 bbl	Lockheed study used to update SO_x, CO and Hc. (KL-081). Chass and George used to update NO_x (CH-055).
	CO	None	4.3 lb/1000 bbl	
	HC	0.5 lb/1000 bbl	0.8 lb/1000 bbl	
	NO_x	None	18.9 lb/1000 bbl	
Vac distillation column condenser	HC	130 lb/1000 bbl	50 lb/1000 bbl	Original factors misquoted from data sources (AT-040, AM-055).

The hydrocarbon emission factors currently used in AP-42 were also developed in the Los Angeles Joint Project between 1955 and 1958 (AT-040). This study determined the hydrocarbon emission rates to be 0.026 lbs/1000 ft^3 of gas and 142 lbs/1000 bbl of oil. Recent, more extensive studies have been conducted by EPA on hydrocarbon emissions from commercial and industrial boilers (EN-071 Section 1.3 and 1.4). These studies determined the level of hydrocarbon emissions from boilers to be approximately 0.003 lbs/1000 ft^3 of gas and 42 lbs/1000 bbl of oil. Since refinery boilers and heaters operate under similar conditions to industrial boilers, Radian assumed the hydrocarbon emission rates to be similar. The refinery boiler and heater hydrocarbon emission rates were changed to the more recent EPA values presented above.

The EPA and SwRI studies, and EPA compliance test data collected in 1974 by KVB (BA-291) verified the rest of the Los Angeles Joint Project emission factors for boilers and heaters, and these were left unchanged. Two heater tests conducted by Battelle for the EPA reported particulate emissions from oil-fired heaters to be approximately 15 to 20 lbs/1000 bbl. These rates are significantly lower than all other rates reported in available data. Because of the limited extent of these tests it was decided not to change the heater emission rates until more data becomes available.

3.3.2 Catalytic Cracking Emission Factors

The refinery emission factors currently reported in AP-42 for both fluid bed (FCC) and moving bed (TCC) catalytic crackers were primarily developed in the Los Angeles Joint Project (AT-040). However, the particulate and carbon monoxide

emission factors for FCC units were developed from later information gathered by EPA in NSPS studies on FGC units (EN-072). Based on this information, current AP-42 emission factors incorrectly indicate that CO boilers have no impact on either hydrocarbon, aldehyde, or ammonia emissions in FCC regeneration flue gas. A review of EPA information on incinerators equipped with afterburners indicates that hydrocarbons and aldehydes are reduced to negligible quantities by secondary combustion equipment (EN-071, Section 2). With this information as a bases, Radian estimated that the CO boiler will combust the major portion of the hydrocarbon, aldehyde, and ammonia emissions in the regenerator off gas, thus lowering these emissions to negligible levels.

3.3.3 Fluid Coker Emission Factors

The current AP-42 emission factor table for refineries reports that carbon monoxide, hydrocarbon, nitrogen oxide, aldehyde, and ammonia emissions are all negligible for uncontrolled fluid cokers. However, a review of the literature cited as the source for these emission values indicates that only particulate emissions were measured on the uncontrolled fluid coker and that the negligible emission values were measured downstream from a carbon monoxide boiler (JO-086). Based on this information, Radian changed the "negligible" values to "NA" (not available) indicating that no information is available on the emission of carbon monoxide, hydrocarbons, aldehydes, nitrogen oxides, and ammonia from uncontrolled fluid coking units.

The negligible emission status was left unaltered for carbon monoxide, hydrocarbon, aldehyde, and ammonia emissions from fluid coking units equipped with CO boilers. It is very likely that these emissions will be very low, if not negligible.

3.3.4 Compressor Engine Emission Factors

The emission factors currently used in AP-42 for reciprocating compressor engines in refinery service were developed in the Los Angeles Joint Project conducted from 1955 to 1958 (AT-040). More extensive studies were conducted for the American Gas Association by the Southwest Research Institute in 1974 and 1975 (UR-022, DI-142). These SwRI studies investigated carbon monoxide, hydrocarbon, and nitrogen oxide emissions from reciprocating compressor engines in the gas industry. The test results obtained by SwRI indicated that the Joint Project emission factors were low for all three pollutants. Radian reviewed the SwRI testing program and found it to be a thorough and accurate study. It was decided to substitute its results for the reciprocating compressor engine emission factors currently used by AP-42.

The SwRI studies also investigated SO_x, CO, hydrocarbon, and NO_x emissions from turbine compressor engines. These emission factors are reported in Section 3.3.2 of AP-42 and are added to the refinery emission factor table, Table 9.1-1.

3.3.5 Blowdown System Emission Factors

The emission factor currently presented in AP-42 for refinery blowdown systems was developed in the Los Angeles Joint Project between 1955 and 1958. The joint project found that

uncontrolled blowdown system emissions averaged 300 lbs of hydrocarbons per thousand barrels of refinery feed. If the hydrocarbon vapors were flared or processed in vapor recovery systems, these emissions were reduced to 5 lbs per thousand barrels of refinery feed (AT-040).

However, the Lockheed Missile and Space Company has recently completed a study of blowdown systems for the EPA (KL-081). This study was conducted with the assistance of the American Petroleum Institute and eighteen refineries. The study results indicate that in today's average refinery, 580 lbs of hydrocarbons per thousand barrels of refinery feed are vented to the blowdown system. In all cases studied, these blowdown effluents are flared instead of vented to the atmosphere. The Lockheed study also measured the sulfur oxide, carbon monoxide, and hydrocarbon emissions from the flare. Because of the greater applicability of the Lockheed study to today's refineries, Radian updated the refinery blowdown system emission factors by using the Lockheed study results.

No testing information is available on the level of NO_x emissions from flares. Radian estimated nitrogen oxide emissions from blowdown flares using the results of a nitrogen oxide emission study conducted by Chass and George in 1958 (CH-055). The Chass and George study was not specific to flares but dealt with general combustion sources.

3.3.6 Vacuum Distillation Column Condenser Emission Factors

Radian changed the emission factors for vacuum distillation column condensers from a value of 130 lbs of hydrocarbons per thousand barrels of vacuum column feed to a value of 50 lbs of hydrocarbons per thousand barrels of vacuum

column feed. AP-42 reports that the current emission factor of 130 lbs/1000 bbl of vacuum unit feed was developed by the Los Angeles Joint Project Study. A review of the Joint Project findings indicates that the range of emissions was from 0 to 130 lbs of hydrocarbons/1000 bbl of vacuum unit feed (AT-040, AM-055). However, most emissions fell in a range of 15 to 50 lbs/1000 bbl with the average being close to the higher figure.

In addition to revising the vacuum distillation column condenser emission factor, Radian also added a factor in the units of 18 lbs of hydrocarbons/1000 bbl of refinery feed. Radian arrived at this factor using the typical vacuum unit feed to refinery feed ratio experienced in today's refinery (CA-339). Reporting the vacuum distillation column condenser emission factors in these units (in addition to the original units) will increase the utility of the factors in cases where only the refinery capacity is known.

3.3.7 Fugitive Emission Factors

Radian made no changes in the numerical values of the emission factors reported in AP-42 for fugitive emission sources. All values were checked against both the original findings of the Joint Project (AT-040) and recent findings from petroleum company testing (WO-099). The recent data on fugitive emission rates indicate that good maintenance practices result in lower emission factors than the current AP-42 factors. But there is insufficient data for Radian to generate new factors.

However, Radian did change the format of the fugitive emission factor table. Not only did Radian report the uncontrolled emission rates as before, but Radian also added the controlled emission rates where available and listed the applicable control technology. Radian also reported many of the

fugitive emission factors in alternate units. As an example, emissions from process drains and wastewater separators had been reported in only units of "lbs of hydrocarbons per thousand gallons of wastewater". Radian also reported the emission factor in units of "lbs of hydrocarbons per thousand barrels of refinery capacity". Presenting the emission factors in several units greatly increases their versatility.

3.3.8 Methane/Non-methane Hydrocarbons

Radian conducted a literature study to determine what portion of the various refinery hydrocarbon emissions are methane. It has been determined that methane does not contribute significantly to the formation of photochemical oxidants or to smog. However very little information was available on the composition of individual refinery emissions. In a study for EPA, TRW has reported that the overall composition of refinery hydrocarbon emissions in the Los Angeles area is 0.3 wt % methane and 99.7 wt % non-methane (TR-107). Rockwell International has also investigated the hydrocarbon emissions from cat cracker regenerators and found them to contain less than 1% methane and greater than 99% non-methane hydrocarbons (GR-360). No other hydrocarbon composition information was available for specific refinery emission sources, although some information was available for similar emission sources in other industries. Another point Radian considered is that much more extensive data is currently being collected by Radian for the EPA on another program. This data includes the methane concentration in hydrocarbon emissions from numerous refinery emission sources. The data from this program will be included in AP-42 at the completion of the program. For these reasons, it was decided not to attempt to develop methane/non-methane compositions for specific refinery emissions. But Radian simply reported the overall methane/non-methane composition of refinery emissions in this revision of the refinery section of AP-42.

3.4 Data Supplied by EPA

Five sets of emission data were received from the National Air Data Branch of EPA for inclusion in this study where applicable. Much of this information was found to be incomplete or insufficient, for the development of new emission factors. However, test data collected by KVB did prove to be very helpful in verifying the accuracy of existing emission factors. Table 3.4-1 summarizes the test data received from the EPA.

TABLE 3.4-1. DATA SUPPLIED BY EPA

Source of Test Data	Emission Source	Emissions
Lace Engineering	Furnace	SO_2
Texas Air Control Board	CO Boiler	Particulates & SO_2
Battelle Research Labs	Crude Heater	Particulates & SO_2
Battelle Research Labs	CO Boiler	Particulates & SO_2
KVB	Furnaces & Boilers	NO_x

The first set of test data was for sulfur dioxide emissions from a refinery furnace on a HDS depentanizer. These tests were conducted by Lace Engineering at the Cosden Oil and Chemical facility in Big Springs, Texas. The results of the tests basically verified that the SO_2 emissions from a refinery heater or furnace can be calculated directly and accurately from the sulfur level in the fuel.

The second set of test data was sulfur dioxide and particulate emission data from a CO waste heat boiler at the Cosden Oil and Chemical facility in Big Spring, Texas.

Difficulties were encountered with using these test results because the samples were collected downstream of double stage cyclones. No efficiencies were reported for the cyclones and they were reported to be operating improperly. In addition, only one set of particulate and one set of SO_2 tests were made. Because of the many unknown and the limited quantity of data, it was decided not to use these test results to modify the existing EPA CO boiler emission factors. The EPA factors are based on a much larger quantity of test results collected under more controlled test conditions.

The third set of test data was collected by Battelle Laboratories on a crude oil heater in Shell Oil Company's Anacortes, Washington refinery. The sulfur dioxide emission data again verified the accuracy of using a material balance for calculating sulfur dioxide emission rates from the sulfur content of the fuel. Two of the particulate test results were not useable because of mixed fuel firing and difficulties in assessing pollutant contributions by each fuel. The remaining two particulate test results indicated particulate emissions from fuel oil combustion are 0.37 and 0.45 lbs/1000 gallons of fuel. These two values are significantly lower than the 10-20 lbs/1000 gallons reported in most other test results available. Further investigation did not reveal the reason for these largely varying values. It was decided that these two test values were insufficient information to revise the existing EPA emission factors.

The fourth set of test data were particulate and sulfur dioxide emissions from a CO waste heat boiler at Texaco's Anacortes, Washington refinery. These tests were also conducted by Battelle Laboratories. Due to heavy firing of auxiliary oil and gas fuels, it was not possible to accurately determine

the contribution of each fuel to the net pollutants in the stack gas.

The fifth set of data was a collection of nitrogen oxide emission results collected by KVB for several West Coast refineries. The data and test conditions for each of these emission rates were in various states of completeness. The three emission sources burning a single fuel and having complete test information indicated NO_x emissions from refinery fuel oil boilers ranged from 50 to 60 lbs per 1000 gallons of fuel oil. This was found to be within the same range of the currently used EPA emission factor of 2900 lb/1000 bbl (87 lb/1000 gal). The high dependence of NO_x emission rate on combustion conditions makes it difficult to develop emission factors with greater accuracy than exhibited by these test results.

4.0 TEST PLAN DEVELOPMENT

Many of the emission factors presented in AP-42 for refinery emission sources are inaccurate. Depending on the process, actual emissions may differ by as much as an order of magnitude from the values calculated using AP-42. However, not all of these inaccurate emission factors will warrant testing programs initially. Some refinery emission sources with inaccurate emission factors are not widely used or are currently being phased out of the petroleum industry. For other emission sources the accuracy of the factors cannot be improved because of the erratic nature of the source's emission rates. And, because of high sampling costs, it may not be cost effective to sample some refinery emission sources.

This section of the final report discusses the merits of conducting emissions testing programs for various refinery emission sources. Section 4.1 reviews the origin and accuracy of existing emission factors. Section 4.2 discusses the estimated costs associated with testing these emission sources. Finally Section 4.3 suggests a prioritization of refinery emission sources in order of sources most benefited by an emission testing program.

4.1 Emission Factor Background

This section reviews the origin and accuracy of the emission factors currently presented in EPA Document AP-42 for refinery emission sources.

4.1.1 Boilers and Heaters

Emission Impact

Steam boilers and process heaters are used in every major refinery to supply process and utility steam, and to heat process streams. The steam demand for a typical integrated refinery is approximately 40,000 lb/1000 bbl of refinery feed. To generate this amount of steam, a boiler capacity of 53 x 10^6 Btu/1000 bbl of refinery feed would be required. The heat demand for a modern integrated refinery is approximately 270 x 10^6 Btu/1000 bbl of refinery feed. However, older, less efficient refineries may have process heater demands approaching 600 x 10^6 Btu/1000 bbl of refinery feed. The total boiler and heater fuel demand for the typical refinery is approximately 323 x 10^6 Btu/1000 bbl of refinery feed. This fuel demand is generally supplied by refinery fuel gas but may also be supplied by residual oil and other internally produced fuels (BU-185).

Table 4.1-1 presents the estimated emission rates for fuel gas fired boilers and heaters in a typical refinery having a total heat demand of 323 x 10^6 Btu/1000 bbl of refinery feed. As this table indicates, refinery boilers and heaters are potentially a significant contributor to both the sulfur oxide and the nitrogen oxide emissions from refineries. Sulfur contents of fuel gas range from 0 to 1 percent. Sulfur oxide emissions resulting from burning a 1% sulfur fuel gas are approximately 55 lbs/1000 bbl of refinery feed. Nitrogen oxide emissions are approximately 71 lb/1000 bbl of refinery feed.

Emission Factor Accuracy

Emission factors for refinery boilers and heaters have been given an emission factor rating of A, which indicates that

TABLE 4.1-1. PRIORITIZATION OF REFINERY EMISSION SOURCES FOR EMISSION TESTING PURPOSES

		Typical emission rates ($lb/10^3$ bbl refinery feed)					EPA emission factor rating	Potential rating after emission testing	Estimated test program expenses ($)	Comment	Suggested priority
		Part.	SO_x	CO	Hc	NO_x					
1.	Boilers and Heaters	6	55	6	1	71	A	A	100,000	Minimal potential for improving factors	low
2.	Fluid Cat. Cracking (controlled)	13	139	neg	neg	20	B	B	100,000	Minimal potential for improving factors	low
3.	Moving Bed Cat Cracking (controlled)	neg	1	neg	neg	neg	B	B	100,000	Minimal potential for improving factors	low
4.	Fluid Coking Units (controlled)	neg	neg	neg	neg	neg	C	B	100,000	Good potential for improving factors, source is locally significant but not nationally significant	intermediate
5.	Reciprocating Engines	neg	2	6	19	40	B	A	100,000	Good potential for improving factors, major NO_x source, but use is declining	intermediate
6.	Blowdown Systems (w/flare)	neg	27	4	1	19	C	B	100,000	Good potential for improving factors, significant emission source	high
7.	Vac Distillation Column Condensers	-	-	-	18	-	C	B	100,000	Good potential for improving factors, significant emission source	High
8.	Claus Plant Tail Gas (uncontrolled)	neg	115	neg	neg	neg	B	B	100,000	Minimal potential for improving factors, major emission source	low
9.	Storage	-	-	-	470	-	B	A	750,000	Good potential for improving factors, major emission source	high
10.	Loading	-	-	-	37	-	A-B	A	100,000	Marginal potential for improving factors, significant emission source	intermediate
11.	Fugitive	-	-	-	290	-	D	B-C	1,400,000	Excellent potential for improving factors, major emission source	high

they are considered very accurate. Each of the emission factors except for the carbon monoxide and hydrocarbon emission factors were developed in the Los Angeles Joint Project conducted from 1955 to 1958 (AT-040). Subsequent fuel combustion studies and compliance tests conducted through 1974 have verified the boiler and heater emission factors reported by the Los Angeles Joint Project. These studies also indicate that carbon monoxide emissions are approximately 210 lb/1000 bbl of oil burned or 0.02 lb/1000 cu. ft. of gas burned; and that hydrocarbon emissions are approximately 42 lb/1000 bbl of oil burned or 0.003 lb/1000 ft^3 of gas burned.

Merits of Emission Testing

There will be very little value in conducting additional emissions testing on refinery boilers and process heaters because the existing factors are accurate. Inaccuracies in current boiler and heater emission factors are primarily due to variations in operating conditions of the units and not to insufficient source testing. Additional source testing is not expected to change the emission factors significantly.

4.1.2 Catalytic Crackers

Emission Impact

Catalytic cracking is used in nearly every major refinery in the United States. Of this catalytic cracking capacity, over 93 percent is accomplished with fluid catalytic crackers. On a national average 281 bbl of petroleum are processed in fluid catalytic crackers per 1000 bbl of crude oil entering the refinery. The national average moving-bed catalytic cracker feed rate is 21 bbl per 1000 bbl of refinery feed. Typical catalytic cracking emission rates are reported in Table 4.1-1. These rates are based on the average catalytic

cracking capacities and the controlled catalytic cracking emission rates reported in EPA Document AP-42 (EN-071).

The catalytic cracking emission rates presented in Table 4.1-1 indicate that controlled fluid catalytic cracking units represent a major source of particulate, sulfur oxide, and nitrogen oxide emissions within the typical refinery. These emission rates will be almost doubled for those refineries with catalytic cracking capacities of 500 bbl FCC feed per 1000 bbl refinery feed.

Moving bed catalytic cracking units do not normally represent a very significant emission source within the typical refinery because of their limited application and their low emission rates on a per unit size basis.

Emission Factor Accuracy

The EPA emission factors for uncontrolled catalytic cracking units were first developed in the Los Angeles Joint Project which was conducted from 1955 to 1958. Later studies by Ben G. Jones of Phillips Petroleum Company supported the findings of the Joint Project. In 1973 the EPA reported the results of NSPS studies on controlled and uncontrolled fluid catalytic cracking emissions (EN-072). These studies centered on carbon monoxide and particulate emissions. They verified existing factors for uncontrolled sources and contributed to the controlled emission factor values.

Because of their limited use, very little emission data has been collected on moving bed catalytic cracking units.

Radian recommends assigning an emission factor rating of B to catalytic cracking emission factors. Most test results from a broad sampling of catalytic cracking units support the EPA emission factors reported in Table 4.1-1. However, available test data also indicate that emissions from individual catalytic cracking units can vary over a wide range. Therefore, these factors are not very reliable when used to predict the performance of individual units.

Merits of Emission Testing

The merits of conducting an emission test program on catalytic cracking units are very minimal. As mentioned previously, test results indicate that there is a wide range in the actual level of emissions from catalytic cracking units. This range of emission levels can be greater than $\pm$ 50%. Because the inaccuracies in catalytic cracking emission factors are attributable to differences between units, additional emission testing will not significantly improve the accuracy of these emission factors.

4.1.3 Fluid Coking Units

Emission Impact

Fluid coking units are used in many refineries to thermally crack heavy oils into naphthas and carbonaceous coke. The contribution of coking emissions to the total emissions from the typical refinery is negligible (Table 4.1-1). This is due in part to a national fluid coking capacity of only 8 bbl/1000 bbl of refinery capacity. For refineries having fluid coking capacities as high as 380 bbl/1000 bbl of refinery capacity, the fluid coking unit becomes a major source of

particulates and possibly of other criteria pollutants. Even with emission controls, large fluid coking units are a major source of emissions.

Emission Factor Accuracy

The emission factors for fluid coking units are considered to be of average quality and were given an emission factor rating of C. The primary data source for the fluid coking emission factors was a report by Mr. Ben G. Jones on particulate control in Phillips Petroleum Company's Avon, California refinery (JO-086). The study involved a limited number of emission tests conducted on a single fluid coker in 1969 and 1970. Particulates and carbon monoxide were the only pollutants tested. Because only a single fluid coker was tested and there have been design changes in fluid cokers in the past seven years, the potential for a large error exists in the fluid coker emission factor now being used by EPA.

Merits of Emission Testing

There are definite merits in conducting an emission testing program for fluid cokers. Currently, there are no emission factors available for sulfur oxide, nitrogen oxide, and hydrocarbon emissions from fluid cokers. The current particulate and carbon monoxide emission factors can be improved from a rating of C to a rating of B. It is not likely that a single set of emission factors can be developed with an A rating (excellent) because of the emission fluctuations that occur between fluid cokers of various designs and operating conditions.

4.1.4 Reciprocating Engines

Emission Impact

Reciprocating engines fired with natural gas are used in many refineries to run high pressure compressors. The estimated reciprocating engine emissions for a typical refinery are presented in Table 4.1-1. These emission estimates are based on a national average reciprocating engine size of 13.3 MSCF natural gas per thousand barrels of refinery feed (MS-001).

As Table 4.1-1 indicates, reciprocating engines are a major source of both carbon monoxide and nitrogen oxide emissions in the refinery. In many refineries where reciprocating engines play a major role in gas compression these emission contributions may be doubled or tripled. The current trend, however, is towards the decreased use of reciprocating engines. Although natural gas has been a cheap, abundant source of energy, lower reliabilities and increasing problems with the cost and availability of natural gas have decreased the use of reciprocating engines in recent years.

Emission Factor Accuracy

Reciprocating engines have been given an emission factor rating of B (good). The emission factors used for refinery engines prior to this study were developed in the Los Angeles Joint Project conducted between 1955 and 1958 (AT-040). However, reports on the reciprocating engine tests done for the project indicate that they were inconclusive.

More intensive emission studies were conducted by Southwest Research Institute in 1974 and 1975 on nitrogen oxide,

hydrocarbon, and carbon monoxide emission rates (DI-142). These studies found carbon monoxide and nitrogen oxide emissions to be much higher than previously reported by the Joint Project. Hydrocarbon emissions were approximately the same. The Southwest Research Institute emission factors appear to be very good and were incorporated into the AP-42 revisions.

Merits of Emission Testing

Additional source testing of reciprocating engine emissions has very few merits. The major pollutant species in reciprocating engine emissions were included in the recent SwRI studies. These factors are good, and the possibility of increasing their accuracy through additional testing is not definite. Emission rate variations among various engines may be too great to allow improvements in emission factor accuracy.

4.1.5 Blowdown Systems

Emission Impact

Blowdown systems are used in every refinery to safely remove hydrocarbon liquids and vapors from downed or malfunctioning equipment. A typical refinery vents approximately 580 pounds of hydrocarbons into the blowdown system per thousand barrels of refinery feed. Many of the hydrocarbons vented into the blowdown are recovered and recycled. The remainder are commonly flared. Table 4.1-1 presents the emissions resulting from flaring blowdown system hydrocarbons in the typical refinery. Blowdown emissions, when flared, may be a major source of sulfur oxide, carbon monoxide, and nitrogen oxide emissions. If uncontrolled, the blowdown system is a major source of hydrocarbon emissions in the refinery.

Emission Factor Accuracy

The emission factors for blowdown systems were developed by Lockheed Missile and Space Company for the Environmental Protection Agency with the Assistance of the American Petroleum Institute (KL-081). Eighteen refineries were included in the study. The quantities of hydrocarbons reported as being flared ranged from 150 to 1800 pounds per thousand barrels of refinery throughput and averaged approximately 580 pounds per thousand barrels of refinery throughput. Lockheed calculated SO_2 emissions produced by flaring the blowdown gases directly from blowdown gas sulfur levels reported by the refineries. Carbon monoxide and hydrocarbon emissions were calculated by Lockheed from the data of Sussman, et. al., a limited flare study conducted in 1958. The nitrogen oxide emissions were calculated by Radian using information from a nitrogen oxide emission study by Chass and George in 1958 on general combustion sources (CH-055). Because of the wide range in hydrocarbon feed rates to refinery flares, and because of the age of the combustion data on flare emissions, the emission factors for controlled refinery blowdown systems have been assigned an emission factor rating of C (average accuracy).

Merits of Emissions Testing

The emission factors for controlled refinery blowdown systems can be improved significantly by conducting an emission testing program. However, the emission testing program will not be able to improve significantly the accuracy of the estimated rate of hydrocarbon venting into the blowdown system. Actual blowdown rates for the refining industry vary over a very wide range of values. The emission testing program will be most effective in defining the emission rates of combustion products

from known flaring blowdown rates. There is less variation among combustion product emission rates for a given blowdown rate than there is among blowdown rates. It should be noted that conducting flare emission tests may prove to be a very difficult task.

4.1.6 Vacuum Distillation Column Condensers

Emission Impact

Until recently, noncondensable vapors from the vacuum units on vacuum distillation columns have been vented to the atmosphere. Many refineries have now eliminated these emissions completely by venting into either the fuel gas system or the blowdown system. The emission rate of these vapors has been estimated to average 50 lbs per 1000 bbl of reduced crude feed to the vacuum distillation column (AM-055). For the typical refinery this is an equivalent emission rate of 18 lbs per 1000 bbl of crude feed to the refinery. Table 4.1-1 compares the contribution of various emission sources to total refinery emissions, and indicates that vacuum distillation emissions are of secondary importance.

Emission Factor Accuracy

The emission factor for hydrocarbon emission rates from vacuum distillation column condensers has been assigned an emission factor rating of C. This emission factor was developed in the Los Angeles Joint Project conducted between 1955 and 1958 (AT-040, AM-055). Most of the vacuum distillation column emission rates fell in a range from 15 to 50 lbs per 1000 bbl of reduced crude feed to the vacuum distillation column. Emission rates as high as 130 lb per 1000 bbl were measured and the average emission rate was close to the 50 lb per 1000 bbl of vacuum column feed. Since these emission rates have not been

verified in recent years, they may not account for the higher separation efficiency of today's distillation columns and the new types of crude oils being refined today.

Merits of Emission Testing

An emission testing program for vacuum distillation column condensers will likely improve the emission factor accuracy to an emission factor rating of B. However, greater accuracy improvements will be limited by the wide range of emission rates exhibited by vacuum distillation column condensers.

4.1.7 Claus Plant Tail Gas

Emission Impact

Although not discussed in the refinery section of AP-42, the tail gases vented from a Claus sulfur recovery plant are a common refinery emission source. Assuming the imported crude oil refined in the United States (40%) has a sulfur content of 1.5 wt%, and that 80% of this sulfur is routed to a three stage Claus unit with a 96% efficiency, then the average sulfur dioxide emission rate from the typical U.S. refinery is approximately 115 lbs of SO_2 per 1000 bbl of refinery feed. These values indicate that uncontrolled Claus plant tail gas emissions are a very significant source of sulfur dioxide emissions in a refinery processing sour crude oils.

Emission Factor Accuracy

In Section 5.18 of AP-42, the emission factors for Claus plant tail gases have been given an emission factor rating of D. The reasons contributing to this low rating are unknown.

However, a review of emission test data on Claus plants indicates that the accuracy of these emission factors is good. A large number of literature sources are available on sulfur oxide emissions from Claus plants. When applied to refineries, the emission factor for Claus plant tail gas probably has an emission factor rating of B.

Merits of Emission Testing

There is very little accuracy improvement to be gained from conducting an emission source testing program for Claus plant emissions. The Claus process is a well established process for which there is extensive emission data available from literature sources.

4.1.8 Storage and Loading Operations

Emission Impact

All petroleum liquids entering and leaving the petroleum refinery pass through the tank farm area of the refinery. Here they are handled in storage and loading operations. As indicated in Table 4.1-1, storage and loading operations in the typical refinery are estimated to emit 500 pounds of hydrocarbons per thousand barrels of refinery throughput (BU-185). These figures indicate that storage and loading operations are the largest source of hydrocarbon emissions in the refinery.

Emission Factor Accuracy

The primary sources of hydrocarbon emission factors for storage and loading operations are the factors and correlations developed by the Evaporative Loss Committee of API

between 1959 and 1962. These correlations are based on testing results assembled by API. The reported accuracy of these correlations at the time of their development was approximately ±25% for storage operations and ±35% for loading operations. Emission factors for gasoline and crude oil loading into tank trucks and marine vessels have been updated recently as a result of current studies by the petroleum industry and EPA. These factors are expected to have even better accuracy.

Merits of Emission Testing

There have been many significant developments made in recent years on storage tank design, especially in the area of seals for floating-roof tanks. It is likely that the API emission factor correlations do not adequately predict the hydrocarbon emissions from newer storage tanks. Recent test results also indicate that API storage and loading emission correlations do not adequately deal with petroleum liquids having low vapor pressures.

Because loading emission rates have just been updated, there will be very little benefit derived from further testing these emission sources. Storage emission factors will be the most improved by an emission testing program. Testing of storage emission sources will probably be able to improve storage emission factors from an emission factor rating of B to a rating of A.

4.1.9 Fugitive Emission Sources

Emission Impact

The second largest source of hydrocarbon emissions in the petroleum refinery is fugitive emission sources.

Fugitive leaks from miscellaneous valves and fittings in the typical refinery are estimated to be 290 lbs per 1000 bbl of refinery throughput (AT-040).

Emission Factor Accuracy

The accuracy of fugitive emission factors is considered poor. Fugitive emission factors have been given an emission factor rating of D. Most of the emission testing which formed the basis for the fugitive emission factors was conducted in the Los Angeles Joint Project between 1955 and 1958. Fugitive emission rates are very dependent on equipment type, equipment age, housekeeping practices, and frequency of maintenance. Because these parameters have all changed since the Joint Project was conducted, the fugitive emission factors are suspected to be very inaccurate. The results of a testing program conducted by Meteorology Research Inc. for Atlantic Richfield Company also indicate that fugitive emission factors for well maintained facilities are substantially lower than current AP-42 factors (WO-099). The MRI study tested a limited number of valves and pump seals in a well maintained production facility. MRI found that valve leaks average 0.00014 lb/day-valve and pump seal leaks average 0.00085 lb/day-pump. Currently, used factors are 0.15 lb/day-valve and 5 lb/day-seal respectively. Although not conclusive, the MRI tests indicate that current fugitive factors may be inaccurate for well maintained facilities.

Merits of Emission Testing

A well designed test program will be capable of improving the accuracy of current fugitive emission factors. However, the improved fugitive emission factors may still have an error of ±50% to ±75%. Fugitive emission sources are the most difficult for which to develop accurate factors or correlations.

There are numerous fugitive sources of various equipment types in the typical refinery. As a result, the fugitive emission rates will vary widely across the refinery, but the average fugitive emission rates for each refinery should vary less between refineries.

4.2 Sampling Program Costs

The costs associated with sampling emission sources within refineries vary greatly, depending on such factors as accuracy of results, size of sources, difficulty of sampling task, and number of pollutants associated with the source. In this section the problems and estimated costs associated with sampling some of the major refinery emission sources are discussed.

4.2.1 Sampling Strategy

An effective sampling program begins with the establishment of a well designed sampling strategy. The initial step in establishing a sampling strategy is to identify the "choice parameters" associated with the source to be sampled. "Choice parameters" are those variables which directly impact the rate of emissions from the source. Typical choice parameters might include fuel type, unit type, unit size and age, and operating temperatures and pressures. These choice parameters form the source categories which must be included when selecting the sources to be tested. The proper selection of choice parameters is very important to the collection of statistically accurate results.

After the identification of choice parameters, "correlating parameters" must be identified for the emission source to be tested. "Correlating parameters" are additional

variables which have a secondary impact on the emission rate. They will be measured and included in the correlations if necessary. Typical correlating parameters might include refinery location, equipment location or configuration, and possibly some of the choice parameters listed above.

Once the choice and correlating parameters are identified for the emission source, they are used in a statistical experimental design procedure for selecting the specific emission tests to be conducted. The statistical experimental design procedure applies a systematic orderly procedure for selecting the optimum combination of parameters to be tested. This procedure minimizes the number of tests required to obtain statistically accurate results.

4.2.2 Point Source Emissions

Point source emissions are emitted from a limited number of easily identifiable stacks or vents. They include such sources as boiler flue gas stacks and Claus plant tail gas vents. Point sources are the easiest category of refinery emission sources to test because of their limited number and easily identifiable point of emissions. A wide range of pollutants are emitted from refinery point sources; including particulates, sulfur oxides, mercaptans, hydrogen sulfide, nitrogen oxides, carbon monoxide, hydrocarbons (methane and non-methane), aldehydes, and ammonia.

In a program recently conducted for the EPA, Radian Corporation developed the costs for sampling five point sources in a study of sixteen refineries. A statistical analysis of the sources indicated that including sixteen refineries would optimize the cost-effectiveness of collecting accurate emission data.

The cost for the five point source test program was $500,000 or approximately $100,000 per point source (for all 16 refineries). This cost includes setting up the program, sampling, analyzing for seven pollutants, and presenting the results in a final report. This is a typical point source sampling program cost, and many sources will be more expensive or less expensive to test. The cost per point source also drops as the size of the test program increases due to the consolidation of some costs.

4.2.3 Fugitive Source Emissions

Fugitive refinery emission sources are small miscellaneous hydrocarbon leaks scattered throughout the refinery. These emissions are very difficult to identify because they are not normally emitted from a well defined stack or vent. Some examples of fugitive refinery emission sources include waste water drains, cooling towers, valves, and pipe fittings.

In a study for EPA Radian developed the cost for a sampling program to identify the emissions from eleven fugitive emission sources (EPA Contract 68-02-2147). These eleven sources include:

- in-line valves
- open-end valves
- flanges
- pressure-relief devices
- pump seals
- unit drains
- compressor seals
- cooling towers
- wastewater facilities
- ditches
- sumps

Approximately six hundred samples would be collected in sixteen refineries in order to quantify the emissions from these fugitive emission sources. The cost of the fugitive sampling program was estimated to be $1,400,000. Species characterization of the fugitive hydrocarbon emissions was not included in this cost estimate. The estimated time period required for conducting the fugitive sampling program would be 1.25 years.

4.2.4 Tankage Emissions

Storage tank testing costs were not included in either the point source cost estimates or the fugitive source cost estimates. Storage tank testing is very difficult and poses some very unique problems. Refinery storage tanks are generally too large to be tested by enclosing and measuring the emissions directly. They must be tested either by testing scaled down models and scaling up the test results, or by conducting sensitive product sampling and calculating weathering rates based on changes in product composition.

Based on the above tankage testing procedures the cost of a tankage emission testing program is estimated to be approximately $750,000. This cost estimate includes test plan development, sampling, analysis, and reporting of final results.

4.3 Prioritization of Emission Sources

The prioritization of emission sources for the purpose of developing a sampling plan is a very difficult task. Things to be considered in prioritizing emission sources include national impact, regional impact, budget, availability of sampling teams, potential for collecting meaningful results, and growth trends. This section discusses the general prioritization

of refinery emission sources. The two things considered are the relative impact of the source's emissions and the potential for improving current criteria pollutant emission factors. The refinery emission source prioritization presented here does not consider any pollutants other than the five EPA criteria pollutants; particulates, sulfur oxides, carbon monoxide, hydrocarbons, and nitrogen oxides. A distinctly different prioritization order would be generated if toxic or carcinogenic pollutants were to be considered.

4.3.1 High Priority

The highest priority for refinery emission sources is given to emission sources for which an emission testing program will definitely improve the accuracy of currently used emission factors. Sources included in the highest priority category are blowdown systems, vacuum distillation column condensers, storage tanks, and fugitive emissions. Fugitive emission sources are given high priority because they represent the second largest source of refinery emissions and the source with the greatest potential for emission factor improvement. Although storage tanks have a good emission factor rating, they have also been included in the highest priority category. Storage tanks represent the largest source of hydrocarbon emissions in the refinery and small improvements in their emission factor accuracy have significant impact on the accuracy of the total refinery emissions. Although not as large an emission source, blowdown emissions and vacuum distillation column condensers are also considered high priority for testing programs. These two sources have a large potential for accuracy improvement at a relatively lower cost than most of the other sources.

4.3.2 Intermediate Priority

The intermediate priority sources are emission sources for which testing programs will be less cost effective than the testing programs for high priority sources. This lower cost effectiveness may be attributable to either lower potential for improvements in accuracy or to higher testing costs. The three sources which are rated intermediate priority are fluid coking units, internal combustion engines, and loading operations. Fluid coking units are considered intermediate priority because of their low impact on a national level. Although they are high particulate and carbon monoxide emitters, fluid cokers are not used very extensively today. But, they are gaining in popularity and may become significant emission sources in the future. Internal combustion engines are also considered intermediate priority sources. Although internal combustion engines are significant emission sources with a large potential for accuracy improvement, the trend is towards their declining usage. They will be contributing less to refinery emissions in the future. Loading emission sources have been given intermediate priority because of the questionable potential for improving their emission factors. Many loading emission sources have been tested recently and additional testing programs may have only a small effect on current emission factor accuracy.

4.3.3 Low Priority

Low priority ratings have been given to boilers, heaters, fluid bed catalytic crackers, moving bed catalytic crackers, and Claus plant tail gases. Regardless of the emission rates from each of these sources, they were given the low priority rating because of the minimal potential which exists for improving their emission factor by emission testing programs. For some factors, only small improvements can be achieved because

the emission rates are already well characterized. For other inaccurate factors, small potential exists for improvement because they can't be better characterized using simple emission factors. However, emission testing should not be ruled out for these sources. Although accurate factors cannot be developed for some sources, testing often leads to the development of accurate complex correlations which incorporate the important parameters.

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APPENDIX A
REVISED AP-42

9.1	Petroleum Refining
9.1.1	General Description
9.1.2	Process Emission Sources and Control Technology
9.1.3	Fugitive Emission Sources and Control Technology

9.1 PETEOLEUM REFINING[1]

9.1.1 GENERAL DESCRIPTION

The petroleum refining industry is primarily involved in the conversion of crude oil into more than 2500 refined products including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils, and feedstocks for the petrochemical industry. Petroleum refinery activities start with crude storage at the refinery, include all petroleum handling and refining operations, and terminate with storage of the refined products at the refinery.

The petroleum refining industry employs a wide variety of processes for the conversion of crude oil to finished petroleum products. A refinery's processing flow scheme selection is largely determined by the composition of the crude oil feedstock and the chosen slate of petroleum products. The example refinery flow scheme presented in Figure 9.1-1 shows the general processing arrangement used by U.S. refineries for major refinery processes. The arrangement of these processes will vary among refineries and few, if any, refineries employ all of these processes. Petroleum refining processes having direct emission sources are presented in bold line boxes.

In general, refinery processes and operations can be divided into five categories:

1) Separation processes
   a. atmospheric distillation
   b. vacuum distillation
   c. light ends recovery (gas processing)

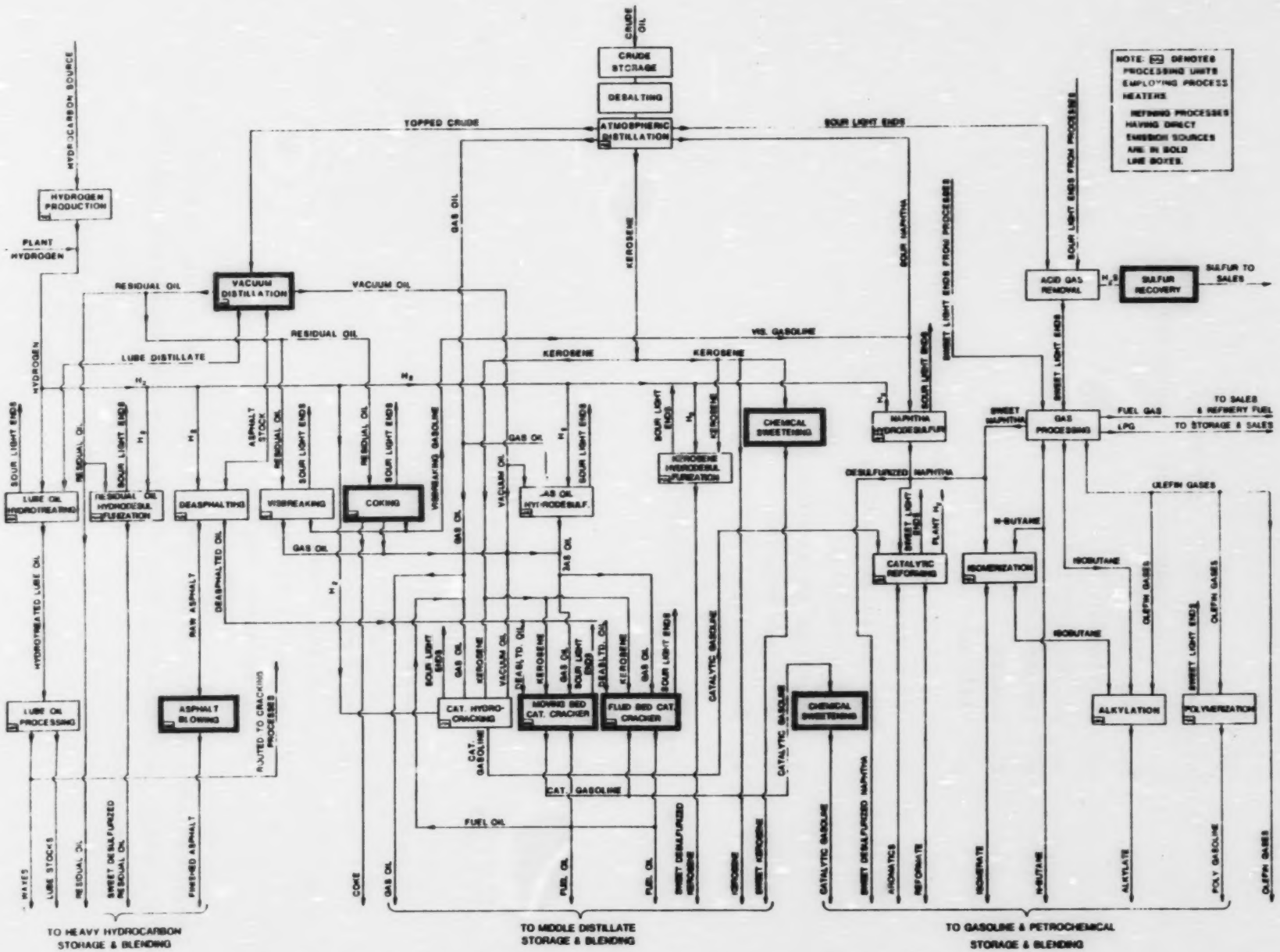

FIGURE 1-1 SCHEMATIC OF AN EXAMPLE INTEGRATED PETROLEUM REFINERY

2) Petroleum conversion processes
   a. cracking (thermal and catalytic)
   b. reforming
   c. alkylation
   d. polymerization
   e. isomerization
   f. coking
   g. visbreaking

3) Petroleum treating processes
   a. hydrodesulfurization
   b. hydrotreating
   c. chemical sweetening
   d. acid gas removal
   e. deasphalting

4) Feedstock and product handling
   a. storage
   b. blending
   c. loading
   d. unloading

5) Auxiliary facilities
   a. boilers
   b. wastewater treatment
   c. hydrogen production
   d. sulfur recovery plant
   e. cooling towers
   f. blowdown system
   g. compressor engines.

These refinery processes are defined in the following section along with their emission characteristics and applicable emission control technology.

Petroleum Separation Processes

The first phase in petroleum refining operations is the separation of crude oil into its major constituents using three petroleum separation processes: atmospheric distillation, vacuum distillation, and light ends recovery. Crude oil consists of a mixture of hydrocarbon compounds including paraffinic, naphthenic, and aromatic hydrocarbons plus small amounts of impurities including sulfur, nitrogen, oxygen, and metals. Refinery separation processes use such techniques as distillation, stripping, and absorption to separate these crude oil constituents into common boiling point fractions.

Petroleum Conversion Processes

Product demand and economic considerations require that less valuable components of crude oil be converted to more valuable products by using the petroleum conversion processes. To meet the demands for high octane gasoline, jet fuel, and diesel fuel, lower value residual oils, fuel oils, and light ends are often converted to gasolines and other light fractions. The cracking, coking, and visbreaking processes are used to break large petroleum molecules into smaller petroleum molecules. On the other hand, polymerization and alkylation processes are used to combine small petroleum molecules into larger ones. Isomerization and reforming processes primarily rearrange the structure of petroleum molecules to produce higher value molecules of a similar molecular size.

Petroleum Treating Processes

Petroleum treating processes stabilize and upgrade petroleum products by separating them from less desirable

petroleum products and by removing objectionable elements from petroleum products and feedstocks. Treating processes used to stabilize products and remove undesirable elements such as sulfur, nitrogen and oxygen include hydrodesulfurization, hydrotreating, chemical sweetening and acid gas removal. Treating processes employed primarily for the separation of petroleum products include such processes as deasphalting. Desalting is used to remove salt, minerals, grit, and water from crude oil feed stocks prior to refining. And asphalt blowing is used to polymerize and stabilize asphalt, improving its weathering characteristics.

Feedstock and Product Handling

The refinery feedstock and product handling operations consist of storage, blending, loading, and unloading activities. All feedstocks entering the refinery and all products leaving the refinery are subject to the refinery handling operations.

Auxiliary Facilities

Auxiliary facilities include a wide assortment of processes and equipment which are not directly involved in the refining of crude oil, but which perform functions vital to the operation of the refinery. These include boilers, wastewater treatment, hydrogen plants, cooling towers, sulfur recovery units, etc. Products from auxiliary facilities (clean water, steam, process heat, etc.) are required by the majority of refinery process units and are not limited to any one part of the refinery.

9.1.2 PROCESS EMISSION SOURCES AND CONTROL TECHNOLOGY

This section presents descriptions of those refining processes which are significant air pollutant contributors. Process flow schemes, emission characteristics, and emission control technology are discussed for each process. Table 9.1-1 lists the emission factors for direct process emissions in the petroleum refinery. The following process emission sources are discussed in this section on petroleum refining emissions:

- vacuum distillation,
- catalytic cracking,
- thermal cracking processes,
- utility boilers,
- heaters,
- compressor engines,
- blowdown systems, and
- sulfur recovery.

Vacuum Distillation

Topped crude withdrawn from the bottom of the atmospheric distillation column is composed of high boiling point hydrocarbons which decompose and polymerize to foul equipment when distilled at atmospheric pressures. In order to further separate topped crude into components, it must be distilled in

TABLE 9.1-1. EMISSION FACTORS FOR PETROLEUM REFINERIES

Type of Process	Particulates	Sulfur Oxides (SO_2)	Carbon Monoxide	Total[a] Hydro-Carbons	Nitrogen Oxides (NO_2)	Aldehydes	Ammonia	Emission Factor Rating
Boilers and Process Heaters[b]								
lb/10^3 bbl oil burned	840	6,720S[c]	210[d]	42[d]	2,900	25	Neg[e]	A
kg/10^3 liters oil burned	2.4	19.2S	0.6[d]	0.12[d]	8.3	0.071	Neg	A
lb/10^3 ft^3 gas burned	0.02	2.s[f]	0.02[d]	0.003[d]	0.23	0.003	Neg	A
kg/10^3 m^3 gas burned	0.32	32s	0.32[d]	0.048[d]	3.7	0.048	Neg	A
Fluid Catalytic Cracking Units[g]								
Uncontrolled								
lb/10^3 bbl fresh feed	242 (93 to 340)[h]	493 (100 to 525)	13,700	220	71.0 (37.1 to 145.0)	19	54	B
kg/10^3 liters fresh feed	0.695 (0.267 to 0.976)	1.413 (0.286 to 1.505)	39.2	0.630	0.204 (0.107 to 0.416)	0.054	0.155	B
Electrostatic Precipitator and CO boiler								
lb/10^3 bbl fresh feed	45[i] (7 to 150)	493 (100 to 525)	Neg	Neg	71.0[j] (37.1 to 145.0)	Neg	Neg	B
kg/10^3 liters fresh feed	0.128 (0.020 to 0.428)	1.413 (0.286 to 1.505)	Neg	Neg	0.204[j] (0.107 to 0.416)	Neg	Neg	B
Moving-Bed Catalytic Cracking Units[b]								
lb/10^3 bbl fresh feed	17	60	3,800	87	5	12	6	B
kg/10^3 liters fresh feed	0.049	0.171	10.8	0.250	0.014	0.034	0.017	B
Fluid Coking Units[k]								
Uncontrolled								
lb/10^3 bbl fresh feed	523	NA[l]	NA	NA	NA	NA	NA	C
kg/10^3 liters fresh feed	1.50	NA	NA	NA	NA	NA	NA	C
Electrostatic Precipitator and CO boiler								
lb/10^3 bbl fresh feed	6.85	NA	Neg	Neg	NA	Neg	Neg	C
kg/10^3 liters fresh feed	0.0196	NA	Neg	Neg	NA	Neg	Neg	C
Delayed Coking Units	NA	NA	NA	NA	NA	NA	NA	NA

(Continued)

TABLE 9.1-1. EMISSION FACTORS FOR PETROLEUM REFINERIES (Continued)

Type of Process	Particulates	Sulfur Oxides (SO_2)	Carbon Monoxide	Total[a] Hydro-Carbons	Nitrogen Oxides (NO_2)	Aldehydes	Ammonia	Emission Factor Rating
Compressor Engines[m]								
Reciprocating Engines								
lb/10^3 ft^3 gas burned	Neg	2s	0.43	1.4	3.4	0.1	0.2	B
kg/10^3 m^3 gas burned	Neg	32s	7.02	21.8	55.4	1.61	3.2	B
Gas Turbines								
lb/10^3 ft^3 gas burned	Neg	2s	0.12	0.02	0.3	NA	NA	B
kg/10^3 m^3 gas burned	Neg	32s	1.94	0.28	4.7	NA	NA	B
Blowdown Systems[n]								
Uncontrolled								
lb/10^3 bbl refinery feed	Neg	Neg	Neg	580	Neg	Neg	Neg	C
kg/10^3 liters refinery feed	Neg	Neg	Neg	1.662	Neg	Neg	Neg	C
Vapor Recovery system and flaring								
lb/10^3 bbl refinery feed	Neg	26.9	4.3	0.8	18.9	Neg	Neg	C
kg/10^3 liters refinery feed	Neg	0.077	0.012	0.002	0.054	Neg	Neg	C
Vacuum Distillation[o] Column Condensers								
Uncontrolled								
lb/10^3 bbl refinery feed	Neg	Neg	Neg	18	Neg	Neg	Neg	C
kg/10^3 liters refinery feed	Neg	Neg	Neg	0.052	Neg	Neg	Neg	C
lb/10^3 bbl vacuum feed	Neg	Neg	Neg	50 (0-130)	Neg	Neg	Neg	C
kg/10^3 liters vacuum feed	Neg	Neg	Neg	0.144	Neg	Neg	Neg	C
Controlled	Neg	Neg	Neg	Neg	Neg	Neg	Neg	C

(Continued)

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TABLE 9.1-1. EMISSION FACTORS FOR PETROLEUM REFINERIES (Continued)

Type of Process	Particulates	Sulfur Oxides (SO_2)	Carbon Monoxide	Total[a] Hydro-Carbons	Nitrogen Oxides (NO_2)	Aldehydes	Ammonia	Emission Factor Rating
Claus Plant and Tail Gas Treatment		See Section 5.18						

[a] Overall, less than 1 percent by weight of the total hydrocarbon emissions are methane.

[b] Reference 2

[c] S = Fuel oil sulfur content (weight percent): factors based on 100 percent combustion of sulfur to SO_2 and assumed density of 336 lb/bbl (0.96 kg/liter).

[d] Carbon monoxide and hydrocarbon factors taken from Tables 1.3-1 and 1.4-1 of this manual.

[e] Negligible emission

[f] s = Refinery gas sulfur content ($lb/1000\ ft^3$): factors based on 100 percent combustion of sulfur to SO_2.

[g] References 2 through 8

[h] Numbers in parenthesis indicate range of values observed.

[i] Under the New Source Performance Standards, controlled FCC regenerators will have particulate emissions lower than 19 $lb/10^3$ bbl fresh feed.

[j] May be higher due to the combustion of ammonia.

[k] Reference 5

[l] NA, Not Available

[m] Reference 9 and 10

[n] Reference 2, 11

[o] Reference 2, 12, 13

a vacuum distillation column at a very low pressure and in a steam atmosphere.

In the vacuum distillation unit topped crude is heated with a process heater to temperatures ranging from 700°F to 800°F. The heated topped crude is flashed into a multi-tray vacuum distillation column operating at vacuums ranging from 0.5 psia to 2 psia. In the vacuum column the topped crude is separated into common boiling point fractions by vaporization and condensation. Stripping steam is normally injected into the bottom of the vacuum distillation column to assist in the separation by lowering the effective partial pressures of the components. Standard petroleum fractions withdrawn from the vacuum distillation column include lube distillates, vacuum oil, asphalt stocks, and residual oils. The vacuum in the vacuum distillation column is normally maintained by the use of steam ejectors but may be maintained by the use of vacuum pumps.

The major sources of atmospheric emissions from the vacuum distillation column are associated with the steam ejectors or vacuum pumps. A major portion of the vapors withdrawn from the column by the ejectors or pumps are recovered in condensers. Historically, the noncondensable portion of the vapors has been vented to the atmosphere from the condensers. There are approximately 50 pounds of noncondensable hydrocarbons per thousand barrels of topped crude processed in the vacuum distillation column.[2,12,13] A second source of atmospheric emissions from vacuum distillation columns is combustion products from the process heater. Process heater requirements for the vacuum distillation column are approximately 37,000 Btu per barrel of topped crude processed in the vacuum column. Process heater emissions and their control are discussed later in this section. Fugitive hydrocarbon emissions from leaking seals and fittings

are also associated with the vacuum distillation unit, but these are minimized by the low operating pressures and low vapor pressures in the unit. Fugitive emission sources are also discussed later in this section.

Control technology applicable to the non-condensable emissions vented from the vacuum ejectors or pumps include venting into blowdown systems or fuel gas systems, and incineration in furnaces or waste heat boilers.[2,12,13] These control technologies are generally greater than 99 percent efficient in the control of hydrocarbon emissions, but they also contribute to the emission of combustion products.

Catalytic Cracking

Catalytic cracking, using heat, pressure, and catalysts, converts heavy oils into lighter products with product distributions favoring the more valuable gasoline and distillate blending components. Feedstocks are usually gas oils from atmospheric distillation, vacuum distillation, coking, and deasphalting processes. These feedstocks typically have a boiling range of 650-1000°F. All of the catalytic cracking processes in use today can be classified as either fluidized-bed or moving bed units.

- Fluidized-bed Catalytic Cracking (FCC) - The FCC process uses a catalyst in the form of very fine particles which act as a fluid when aerated with a vapor. Fresh feed is preheated in a process heater and introducted into the bottom of a vertical transfer line or riser with hot regenerated catalyst. The hot catalyst vaporizes the feed bringing both to the desired reaction temperature (880-980°F). The high activity of modern catalysts causes most of the cracking reactions to take place in the riser as the catalyst and oil mixture flows upward into the

reactor. The hydrocarbon vapors are separated from the catalyst particles by cyclones in the reactor. The reaction products are sent to a fractionator for separation.

The spent catalyst falls to the bottom of the reactor and is steam stripped as it exits the reactor bottom to remove adsorbed hydrocarbons. The spent catalyst is then conveyed to a regenerator. In the regenerator, coke deposited on the catalyst as a result of the cracking reactions is burned off in a controlled combustion process with preheated air. Regenerator temperature is usually 1100 - 1250°F. The catalyst is then recycled to be mixed with fresh hydrocarbon feed.

- Moving-bed Catalytic Cracking (TCC) - In the TCC process catalyst beads (~0.5 cm) flow by gravity into the top of the reactor where they contact a mixed phase hydrocarbon feed. Cracking reactions take place as the catalyst and hydrocarbons move concurrently downward through the reactor to a zone where the catalyst is separated from the vapors. The gaseous reaction products flow out of the reactor to the fractionation section of the unit. The catalyst is steam stripped to remove any adsorbed hydrocarbons. It then falls into the regenerator where coke is burned from the catalyst with air. The regenerated catalyst is separated from the flue gases and recycled to be mixed with fresh hydrocarbon feed. The operating temperatures of the reactor and regenerator in the TCC process are comparable to those in the FCC process.

Air emissions from catalytic cracking processes are 1) combustion products from process heaters, and 2) flue gas from catalyst regeneration. Emissions from process heaters are dis-

cussed later in this section. Emissions from the catalyst regenerator include hydrocarbons, oxides of sulfur, ammonia, aldehydes, oxides of nitrogen, cyanides, carbon monoxide, and particulates (Table 9.1-1). The particulate emissions from FCC units are much greater than those from TCC units because of the higher catalyst circulation rates used.[2,3,5]

FCC particulate emissions are controlled by cyclones and/or electrostatic precipitators. Particulate control efficiencies are as high as 80 to 85 percent.[3,5] Carbon monoxide wasteheat boilers reduce the carbon monoxide and hydrocarbon emissions from FCC units to negligible levels.[3] TCC catalyst regeneration produces similar pollutants to FCC units but in much smaller quantities (Table 9.1-1). The particulate emissions from a TCC unit are normally controlled by high efficiency cyclones. Carbon monoxide and hydrocarbon emissions from a TCC unit are incinerated to negligible levels by passing the flue gases through a process heater fire-box or smoke plume burner. In some installations sulfur oxides are removed by passing the regenerator flue gases through a water or caustic scrubber.[2,3,5]

Thermal Cracking

Thermal cracking processes include visbreaking and coking which break heavy oil molecules by exposing them to high temperatures.

- Visbreaking - Topped crude or vacuum residuals are heated and thermally cracked (850-900°F, 50-250 psig) in the visbreaker furnace to reduce the viscosity or pour point of the charge. The cracked products are quenched with gas oil and flashed into a fractionator. The vapor overhead from the fractionator is separated into light distillate products.

A heavy distillate recovered from the fractionator liquid can be used as a fuel oil blending component or used as catalytic cracking feed.

• Coking - Coking is a thermal cracking process which is used to convert low value residual fuel oil to higher value gas oil and petroleum coke. Vacuum residuals and thermal tars are cracked in the coking process at high temperature and low pressure. Products are petroleum coke, gas oils and lighter petroleum stocks. Delayed coking is the most widely used process today, but fluid coking is expected to become an important process in the future.

In the delayed coking process heated charge stock is fed into the bottom section of a fractionator where light ends are stripped from the feed. The stripped feed is then combined with recycle products from the coke drum and is rapidly heated in the coking heater to a temperature of 900-1100°F. Steam injection is used to control the residence time in the heater. The vapor-liquid feed leaves the heater, passing to a coke drum where, with controlled residence time, pressure (25-30 psig), and temperature (750°F), it is cracked to form coke and vapors. Vapors from the drum return to the fractionator where the thermal cracking products are recovered.

In the fluid coking process, typified by Flexicoking, residual oil feeds are injected into the reactor where they are thermally cracked, yielding coke and a wide range of vapor products. Vapors leave the reactor and are quenched in a scrubber where entrained coke fines are removed. The vapors are then fractionated. Coke from the reactor enters a heater and is devolatilized. The volatiles from the heater are treated for fines removal and sulfur removal to yield a particulate free,

low sulfur fuel gas. The devolatilized coke is circulated from the heater to a gasifier where 95% of the reactor coke is gasified at high temperature with steam and air or oxygen. The gaseous products and coke from the gasifier are returned to the heater to supply heat for the devolatilization. These gases exit the heater with the heater volatiles through the same fines removal and sulfur removal processes.

From available literature it is unclear what emissions are released and where they are released. Air emissions from thermal cracking processes include coke dust from decoking operations, combustion gases from the visbreaking and coking process heaters, and fugitive emissions. Emissions from the process heaters are discussed later in this section. Fugitive emissions from miscellaneous leaks are significant because of the high temperatures involved, and are dependent upon equipment type and configuration, operating conditions, and general maintenance practices. Fugitive emissions are also discussed later in this section. Particulate emissions from delayed coking operations are potentially very significant. These emissions are associated with removing the coke from the coke drum and subsequent handling and storage operations. Hydrocarbon emissions are also associated with cooling and venting the coke drum, prior to coke removal. However, comprehensive data for delayed coking emissions have not been included in available literature.[4,5]

Particulate emission control is accomplished in the decoking operation by wetting down the coke.[5] Generally, there is no control of hydrocarbon emissions from delayed coking. However, some facilities are now collecting coke drum emissions in an enclosed system and routing them to a refinery flare.[4,5]

Utilities Plant

The utilities plant supplies the steam necessary for the refinery. Although the steam can be used to produce electricity by throttling through a turbine, it is primarily used for heating and separating hydrocarbon streams. When used for heating, the steam usually heats the petroleum indirectly in heat exchangers and returns to the boiler. When used in direct contact operations the steam can serve as a stripping medium, or a process fluid. Steam may also be used in vacuum ejectors to produce a vacuum.

The emissions from boilers, and applicable emission control technology are discussed in much greater detail in Chapter 1.0.

Sulfur Recovery Plant

Sulfur recovery plants are used in petroleum refineries to convert hydrogen sulfide (H_2S) separated from refinery gas streams into the more disposable by-product, elemental sulfur.

The emissions from sulfur recovery plants and their control are discussed in Section 5.18.

Blowdown System

The blowdown system provides for the safe disposal of hydrocarbons (vapor and liquid) discharged from pressure relief devices.

Most refining processing units and equipment subject to planned or unplanned hydrocarbon discharges are manifolded into a collection unit, called the blowdown system. By using a series of flash drums and condensers arranged in decreasing pressure, the blowdown is separated into vapor and liquid cuts. The separated liquid is recycled into the refinery. The gaseous cuts can either be smokelessly flared or recycled.

Uncontrolled blowdown emissions primarily consist of hydrocarbons, but can also include any of the other criteria pollutants processed by the refinery. The emission rate in a blowdown system is a function of the amount of equipment manifolded into the system, the frequency of equipment discharges, and the blowdown systems's controls.

Emissions from the blowdown system can be effectively controlled by combustion of the non-condensables in a flare. To obtain complete combustion or smokeless burning, (as required by most states) steam is injected in the combustion zone of the flare to provide turbulence and to inspirate air. Steam injection also reduces NO_x emissions by lowering the flame temperature. Controlled emissions are listed in Table 9.1-1.[2,11]

Process Heaters

Process heaters (furnaces) are used extensively in refineries to supply the heat necessary to raise the temperature of feed materials to reaction or distillation temperature. They are used in many processes throughout the refinery.

Process heaters are designed to raise petroleum fluid temperatures to a maximum of about 950°F. The fuel burned may

be refinery gas, natural gas, residual fuel oils, or combinations, depending on the economics, operating conditions, and pollution requirements. The process heaters may also use carbon monoxide-rich regenerator flue gas as fuel.

All the criteria pollutants are emitted from process heaters. The quantity of these emissions is a function of the type of fuel burned, the nature of the contaminants in the fuel, and the heat duty of the furnace. Sulfur oxide emissions can be controlled by fuel desulfurization or flue gas treatment. Carbon monoxide and hydrocarbons can be limited by better combustion efficiency. Current technology is investigating four general techniques or modifications for the control of NO_x emissions. These include combustion modification, fuel modification, alternate furnace design, and flue gas treatment. Several of these NO_x control techniques are presently being applied to large utility boilers, but their applicability to process heaters is undefined.[2,14]

Compressor Engines

Many older refineries use reciprocating and gas turbine engines fired with natural gas to run high pressure compressors. Natural gas has traditionally been a cheap abundant source of energy. Examples of refining units operating at high pressure include hydrodesulfurization, isomerization, reforming, and hydrocracking units. Internal combustion engines are less reliable and harder to maintain than steam engines or electric motors. For this reason and because of increasing natural gas costs very few such units have been installed in the last few years.

The major source of emissions from compressor engines are combustion products in the exhaust gas. These emissions include carbon monoxide, hydrocarbons, nitrogen oxides, aldehydes, and ammonia. Sulfur oxides may also be present depending on the sulfur content of the natural gas. All of these emissions are significantly higher in exhaust from reciprocating engines than from turbine engines.

The major emission control technique applied to compressor engines is carburetion adjustment similar to that applied on automobiles. Catalyst systems similar to those applied to automobiles may also be effective in reducing emissions but are currently undefined for this application.

9.1.3 FUGITIVE EMISSION SOURCES AND CONTROL EQUIPMENT

This section presents descriptions of refinery processes and operations which are significant sources of fugitive emissions. Process flow schemes, emission characteristics and emission control technology are discussed for each process. Emission factors for both uncontrolled and controlled fugitive emission sources are listed in Table 9.1-2. The following fugitive emission sources are discussed in this section on petroleum refining emissions:

- wastewater systems,
- cooling towers,
- pipeline fittings,
- relief valves,
- pump and compressor seals,
- asphalt blowing,
- blind changing,
- sweetening,

TABLE 9.1-2. FUGITIVE HYDROCARBON EMISSION FACTORS FOR PETROLEUM REFINERIES [a,b]
EMISSION FACTOR RATING: D

Emission Source	Emission Factor Units	Uncontrolled Emissions	Controlled Emissions	Applicable Control Technology
Process drains and waste water separators	lb/10^3 gal wastewater	5	0.2	Vapor recovery systems and/or separator covers
	kg/10^3 liters wastewater	0.6	0.024	
	lb/10^3 bbl refinery feed [c]	200	10	
	kg/10^3 liters refinery feed	0.6	0.03	
Cooling towers	lb/10^6 gal cooling water	6	NA [d]	Minimization of oil leaks into cooling water system through good housekeeping and maintenance
	kg/10^6 liters cooling water	0.7	NA	
	lb/10^3 bbl refinery feed	10	NA	
	kg/10^3 liters refinery feed	0.03	NA	
Pipeline valves and flanges	lb/day-valve	0.15	NA	Good housekeeping and maintenance
	kg/day-valve	0.07	NA	
	lb/10^3 bbl refinery feed	28	NA	
	kg/10^3 liters refinery feed	0.08	NA	
Vessel relief valves	lb/day-valve	2.4	Neg	Rupture discs up stream of relief valves and/or vent to blowdown system
	kg/day-valve	1.1	Neg	
	lb/10^3 bbl refinery feed	11	Neg	
	kg/10^3 liters refinery feed	0.03	Neg	
Pump seals	lb/day-seal	5	3	Mechanical seals, dual seals, purged seals
	kg/day-seal	2.3	1.4	
	lb/10^3 bbl refinery feed	17	10	
	kg/10^3 liters refinery feed	0.05	0.03	

(Continued)

TABLE 9.1-2. FUGITIVE HYDROCARBON EMISSION FACTORS FOR PETROLEUM REFINERIES
EMISSION FACTOR RATING: D (Continued)

Emission Source	Emission Factor Units	Uncontrolled Emissions	Controlled Emissions	Applicable Control Technology
Compressor Seals	lb/day-seal	9	NA	Mechanical Seals, dual seals, purged seals
	kg/day-seal	4	NA	
	lb/10^3 bbl refinery feed	5	NA	
	kg/10^3 liters refinery feed	0.014	NA	
Asphalt blowing	lb/ton of asphalt	60	Neg	Scrubber, incinerator
	kg/metric ton of asphalt	30	Neg	
Blind changing	lb/10^3 bbl refinery feed	0.3	Neg	Line flushing, use of "line" blinds, blind insulation with gate valves
	kg/10^3 liters refinery feed	0.001	Neg	
Miscellaneous: sampling, non-asphalt blowing, (sweetening), purging etc.	lb/10^3 bbl refinery feed	10	NA	Good housekeeping and maintenance
	kg/10^3 liter refinery feed	0.03	NA	
Storage	See Section 4.3			
Loading	See Section 4.4			

[a] References 2, 4, 12, 13

[b] Overall, less than 1 percent by weight of total hydrocarbon emissions are methane.

[c] Refinery feed is defined as the crude oil feed rate to the atmospheric distillation column.

[d] NA - These factors are not available.

- storage, and
- transfer operations.

Sweetening

Sweetening of distillates is accomplished by the conversion of mercaptans to alkyl-disulfides in the presence of a catalyst. The conversion process may be followed by an extraction step for the removal of the alkyl-disulfides.

In the conversion process sulfur is added to the sour distillate with a small amount of caustic and air. This mixture is then passed upward through a fixed-bed catalyst countercurrent to a flow of caustic entering at the top of the vessel.

In the conversion and extraction process the sour distillate is prewashed with caustic and then is contacted with a solution of catalyst and caustic in the extractor. The extracted distillate is then contacted with air to convert mercaptans to disulfides. After oxidation the distillate is settled, inhibitors are added, and the distillate is sent to storage. Regeneration is accomplished by mixing caustic from the bottom of the extractor with air and separating the disulfides and excess air.

The major source of air emissions are fugitive hydrocarbon emissions generated when the distillate product is contacted with air in the "air blowing" step. These emissions are dependent upon equipment type and configuration as well as on operating conditions and maintenance practices.[4]

Asphalt Blowing

The asphalt blowing process polymerizes asphaltic residual oils by oxidation, increasing their melting temperature and hardness to achieve an increased resistance to weathering.

The oils containing a large quantity of polycyclic aromatic compounds (asphaltic oils) are oxidized by blowing heated air through a preheated batch mixture or, in the continuous process, by passing hot air countercurrent to the oil flow. The reaction is exothermic, and quench steam is sometimes needed for temperature control. In some cases ferric chloride or phosphorus pentoxide is used as a catalyst to increase the reaction rate and impart special characteristics to the asphalt. Blowing is stopped when the asphalt reaches the desired product specifications.

Air emissions from asphalt blowing are primarily fugitive hydrocarbon vapors vented with the blowing air. The quantities of emissions are small because of the prior removal of volatile hydrocarbons in the distillation units, but the emissions may contain hazardous polynuclear organics.[2,4,13,15]

Emissions from asphalt blowing can be controlled to negligible levels by vapor scrubbing, by incineration, or by a combination of the two.[4,13]

Storage

All refineries have a feedstock and product storage area, termed a "tank farm", which provides surge storage capacity to insure smooth, uninterrupted refinery operations. Individual storage tank capacities range from less than 1000

barrels to more than 500,000 barrels, and total tank farm storage capacities commonly range from several days to several weeks. Storage tank designs, emissions, and emission control technologies are discussed in detail in Section 4.3.

Transfer Operations

Although most refinery feedstocks and products are transported by pipeline, many feedstocks and products are transported by trucks, rail cars, and marine vessels. The refinery feedstocks and products are transferred to and from these transport vehicles in the refinery tank farm area using specialized pumps and piping systems. The emissions from transfer operations and applicable emission control technology are discussed in much greater detail in Section 4.4.

Wastewater Treatment Plant

All refineries employ some form of wastewater treatment to upgrade the quality of water effluents such that they can be safely returned to the environment or reused within the refinery.

The design of wastewater treatment plants is complicated by the diversity of refinery pollutants including oil, phenols, sulfides, dissolved solids, suspended solids, and toxic chemicals. Although the wastewater treatment processes employed by refineries vary greatly, they generally include neutralizers, oil-water separators, settling chambers, clarifiers, dissolved air flotation systems, coagulators, aerated lagoons, and activated sludge ponds. Refinery water effluents are collected from various processing units and conveyed through sewers and ditches to the wastewater treatment plant. Most of the wastewater treatment processing occurs in open ponds and tanks.

The main components of atmospheric emissions from wastewater treatment plants are fugitive hydrocarbons and dissolved gases which evaporate from the surfaces of wastewaters residing in open process drains, wastewater separators, and wastewater ponds (Table 9.1-2). Treatment processes which involve the extensive contacting of wastewater with air such as aeration ponds and dissolved air flotation create an even greater potential for atmospheric emissions.

The control of wastewater treatment plant emissions involves covering wastewater systems where emission generation is greatest (such as covering API separators and settling basins) and removing dissolved gases from wastewater streams with sour water strippers and phenol recovery units prior to their contact with the atmosphere. These control techniques can potentially achieve greater than 90 percent reduction of wastewater system emissions.[13]

Cooling Towers

Cooling towers are used extensively in refinery cooling water systems to transfer waste heat from the cooling water to the atmosphere. The only refineries not employing cooling towers are those with once through cooling. The increasing scarcity of large water supplies required by once through cooling is contributing to the disappearance of that form of refinery cooling. In the cooling tower warm cooling water returning from refinery processes is contacted with air by cascading through packing. Heat in the cooling water is transferred to the air. Cooling water circulation rates for refineries commonly range from 0.3 to 3.0 gpm/bbl per day of refinery capacity.[2,16]

Atmospheric emissions from the cooling tower consist of fugitive hydrocarbons and gases stripped from the cooling water as the air and water come into contact. These contaminants enter the cooling water system from leaking heat exchangers and condensers. Although the predominant contaminant in cooling water is hydrocarbons, dissolved gases such as H_2S and NH_3 may also be found in cooling water (Table 9.1-2).[2,4]

Control of cooling tower emissions is accomplished by reducing contamination of cooling water through the proper maintenance of heat exchangers and condensers. The effectiveness of cooling tower controls is highly variable, depending on refinery configuration and existing maintenance practices.[4]

Miscellaneous Fugitive

Miscellaneous fugitive emission sources are generally defined as hydrocarbon emission sources which are not associated with a particular refining process, but which are scattered throughout the refinery. Fugitive emission sources include valves, flanges, pipe fittings, pump and compressor seals, blind changing, and sample line purging. Hydrocarbon emissions from fugitive emission sources are attributable to the evaporation of leaked or spilled petroleum liquids and gases. Normally the control of fugitive emissions involves the minimization of leaks and spills through equipment changes, procedural changes, and improved housekeeping and maintenance practices. Fugitive emissions which are localized can often be controlled by incineration or vapor recovery systems.

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